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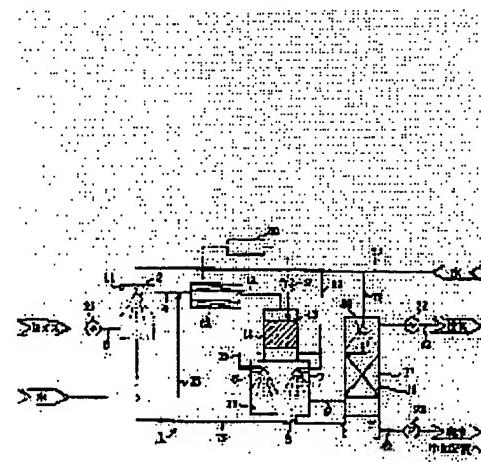
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## (54) TREATMENT OF PERFLUORIDE AND TREATING DEVICE THEREFOR

### (57)Abstract:

PROBLEM TO BE SOLVED: To prevent the clogging of a catalyst bed to improve the decomposition reaction of a perfluoride.

SOLUTION: A waste gas containing a perfluoride (PFC) and SiF<sub>4</sub> and discharged from a semiconductor producing device is introduced into a pre-spray 11 and brought into contact with water to convert Si to SiO<sub>2</sub> to remove. The waste gas discharged from the pre-spray 11 is mixed with a reaction water and heated to 700°C



by a heater 12. After that, the gas containing PFC is introduced into the catalyst bed 14 filled with an alumina based catalyst. The PFC is decomposed by the catalyst into HF and CO<sub>2</sub>. The high temp. waste gas discharged from the catalyst bed 14 and containing CO<sub>2</sub> and HF is cooled in a cooling device and introduced into a removing device 17 to remove HF. Because Si in the waste gas is removed, the clogging of the catalyst bed caused by SiO<sub>2</sub> generated by the reaction of SiF<sub>4</sub> with the reaction water is prevented.

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**CLAIMS**

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**[Claim(s)]**

[Claim 1] Remove a part for this silicon from exhaust gas containing fault fluoride and silicon, and exhaust gas containing said fault fluoride in which either water and a steam were added is heated after that, A disposal method of fault fluoride which cools and exhausts exhaust gas containing cracked gas which supplied a catalyst bed with which a catalyst was filled up, disassembled said fault fluoride contained in said exhaust gas according to said catalyst, and was produced by disassembly of said fault fluoride.

[Claim 2] A disposal method of fault fluoride of claim 1 which performs said heating so that temperature of said exhaust gas may be not less than 650 \*\*.

[Claim 3] A disposal method of fault fluoride of claim 2 in which said exhaust gas is heated by range which are 650 \*\* - 750 \*\*.

[Claim 4] A disposal method of fault fluoride of claim 1 which removes acid gas from said cooled exhaust gas, or claim 2.

[Claim 5] A disposal method of fault fluoride of claim 1 which performs removal of silicon from said exhaust gas by contacting exhaust gas and water containing said silicon.

[Claim 6] A disposal method of fault fluoride of claim 5 which performs cooling of exhaust gas containing said cracked gas by contact with said exhaust gas and cooling water.

[Claim 7] A disposal method of fault fluoride of claim 6 to which mixed water of said cooling water which cooled exhaust gas is contacted characterized by comprising the following.

Removal of silicon from said exhaust gas is performed using the 1st silicon stripper and the 2nd silicon stripper, Said exhaust gas discharged from said 1st silicon stripper is supplied to said 2nd silicon stripper, water and said exhaust gas are contacted within said 2nd silicon stripper, and it is said exhaust gas within said 1st silicon stripper.

Wastewater discharged from said 1st silicon stripper, and said cracked gas.

[Claim 8]A disposal method of fault fluoride of claim 1 generated by heat exchange of said exhaust gas and water in which said steam was discharged from said catalyst bed.

[Claim 9]A disposal method of fault fluoride of claim 1 in which said catalyst is an alumina system catalyst.

[Claim 10]A disposal method of fault fluoride of either claim 1 which is the exhaust gas with which said exhaust gas was discharged from a semiconductor manufacturing device thru/or claim 9.

[Claim 11]A fault fluoride processing unit comprising:

A silicon stripper which removes a part for this silicon from exhaust gas containing fault fluoride and silicon.

Heating apparatus which heats exhaust gas containing said fault fluoride in which either water and a steam were added after discharge of said silicon stripper.

A catalyst bed with which a catalyst which disassembles fault fluoride contained in said exhaust gas discharged from said heating apparatus was filled up.

A cooling system which cools said exhaust gas discharged from said catalyst bed.

[Claim 12]A fault fluoride processing unit of claim 11 characterized by comprising the following.  
A thermometric element which detects temperature of said exhaust gas discharged from said catalyst bed.

A control device which controls said heating apparatus based on measurement temperature of this thermometric element.

[Claim 13]A fault fluoride processing unit of claim 11 provided with an acid gas stripper which removes acid gas contained in said exhaust gas discharged from said cooling system.

[Claim 14]A fault fluoride processing unit of claim 11 with which said silicon stripper is provided with a spray device which carries out the spray of the water into said exhaust gas.

[Claim 15]A fault fluoride processing unit of claim 14 provided with a spray device with which said cooling system carries out the spray of the cooling water which cools said exhaust gas.

[Claim 16]The 1st silicon stripper which has the 1st spray that carries out the spray of the water into said exhaust gas with which said silicon stripper was supplied, And the 2nd silicon stripper which has the 2nd spray that carries out the spray of the water is included in said exhaust gas supplied from said 1st silicon stripper, A fault fluoride processing unit of claim 15 provided with a water supplying means which leads water discharged from said 1st silicon stripper, and water discharged from said cooling system to said 1st spray.

[Claim 17]A fault fluoride processing unit of claim 11 which made integral construction said warmer, a reactor which contains said catalyst bed, and said cooling system at this order.

[Claim 18]A fault fluoride processing unit of claim 17 which provided a horizontal type in which

said integral construction arranges horizontally said warmer, said reactor, and said cooling system, and a baffle member which intercepts a flow of nothing and fault fluoride which is not disassembled into the upper part of said catalyst bed.

[Claim 19]A fault fluoride processing unit of claim 11 which provided a heat exchanger which performs heat exchange between exhaust gas and water which were discharged from said catalyst bed, and generates said steam between said catalyst bed and said cooling system.

[Claim 20]A fault fluoride processing unit of either claim 11 thru/or claim 19 in which said catalyst with which said catalyst bed was filled up is an alumina system catalyst.

[Claim 21]A flue gas treatment apparatus of a semiconductor manufacturing device characterized by comprising the following.

A silicon stripper which removes this silicon from exhaust gas containing a part for fault fluoride and silicon discharged from a semiconductor manufacturing device.

Heating apparatus which heats exhaust gas containing said fault fluoride in which either water and a steam were added after discharge of said silicon stripper.

A catalyst bed with which a catalyst which disassembles fault fluoride contained in said exhaust gas discharged from said heating apparatus was filled up.

A cooling system which cools said exhaust gas discharged from said catalyst bed.

[Claim 22]A flue gas treatment apparatus of a semiconductor manufacturing device of claim 21 which installed said warmer which made integral construction said warmer, a reactor which contains said catalyst bed, and said cooling system at this order, and was made into integral construction, said reactor, and said cooling system in a building in which said semiconductor manufacturing device is installed.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Field of the Invention]**This invention relates to the disposal method of suitable fault fluoride to apply to processing of the fault fluoride (PFC is called hereafter) which is applied to the disposal method of fault fluoride and its processing unit, especially is contained in the exhaust gas of a semiconductor plant, and its processing unit.

**[0002]**

**[Description of the Prior Art]**In the semiconductor manufacturing process, in the case of CVD processes, such as  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$  etc. are harmless to a human body, there is no explosivity in cleaning gas, and, as for the case of a dry etching process, the easy PFC gas of handling is used for etching gas. These PFC gas is ionized by the plasma discharge of high tension after introducing into an etching device or a CVD system, and performs etching or cleaning of a wafer in the state of an activity radical. However, the gas volume actually consumed in etching or cleaning is a number - tens vol(s)% , and the remainder is discharged out of the system, while it has been unreacted.

**[0003]**Since an atomic radius is small and associative strength of a fluorine atom is strong, PFC which is the compound has stable physical properties. PFC(s) are fault fluorides, such as chlorofluocarbon of FC (fluorocarbon) which does not contain chlorine, or HFC (hydroniumfluorocarbon), nitrogen trifluoride ( $\text{NF}_3$ ), sulfur hexafluoride ( $\text{SF}_6$ ), and show the main PFC name, its physical properties, a using state, etc. in Table 1.

**[0004]****[Table 1]**

表 1

No.	PFCガス	ガスの物性 温暖化係数 大気中寿命(年)	毒性、反応性	日本の消費量 トン/年(94)	主 要 用 途
1	CF <sub>4</sub> (フロン14)	6,300 50,000	不燃性 低毒性	300トン/年(94) 394トン/年(95)	エッチングガス: 75% CVDクリーニングガス: 25%
2	CF <sub>6</sub> (フロン116) (三氟化硫)	12,500 9,720	不燃性 低毒性	4トン/年(94) 200トン/年(95)	P-CVDクリーニングガス CVDクリーニングガス: 92% ICエッチャングガス: 8%
3	NF <sub>3</sub> (フロン23)	1,790	毒性有り	25トン/年(94)	CVDクリーニングガス: 92%
4	CHF <sub>3</sub> (フロン23)	12,100	250	39トン/年(95) 55トン/年(94)	ドライエッチャング エッチャング
5	C <sub>4</sub> F <sub>8</sub> (フロンC318)	8,700	3,200		P-CVDクリーニングガス
6	C <sub>3</sub> F <sub>8</sub> (フロン218)	7,000	2,600		
7	SF <sub>6</sub> (六氟化硫)	24,900	3,200	26トン/年(94)	ドライエッチャング用 CVDクリーニングガス: 10%

[0005]Excluding chlorine, since molecular structure is compact and the associative strength of molecular structure is also strong, PFC exists in stability in the atmosphere for a long time. For example, in 50,000 years and C<sub>2</sub>F<sub>6</sub>, 10,000 years and SF<sub>6</sub> are [ CF<sub>4</sub> ] 3,200. A year and a life are long. However, 6,500 times and C<sub>2</sub>F<sub>6</sub> are 9,200 times, a warming coefficient is large and CF<sub>4</sub> is [ SF<sub>6</sub> ] 23,900 times as compared with CO<sub>2</sub>. For this reason, although there are few

burst sizes compared with CO<sub>2</sub> currently asked for reduction as a cause of global warming, it is concluded that future near discharge regulation is inevitable. In this case, the exhaust countermeasure in the semiconductor plant which occupies the great portion of present PFC discharge becomes important.

[0006]In the present semiconductor plant, when based, for example on an etching process, the PFC gas for etching is supplied to a chamber, plasma is impressed to PFC, the part is changed into the high fluorine atom of corrosive action, and a silicon wafer is etched. Although the exhaust gas in a chamber is continuously exhausted with a vacuum pump, the nitrogen gas purge which prevents the corrosion by acid gas is performed. For this reason, 99% of the presentations of exhaust gas are nitrogen, and the remaining 1% is PFC which was not used for etching. After the exhaust gas which went via the vacuum pump is led to an acid duct and removes acid gas, while PFC had been included, it is emitted into the atmosphere.

[0007]The drugs method and the combustion system are used as decomposition art of the conventional PFC. When the former uses special drugs, it is the method of fixing fluoride chemically at about 400-900 \*\*, and since there is no generating of the acid gas by decomposition, flue gas treatment becomes unnecessary. The latter leads PFC gas to a burner and carries out a pyrolysis in not less than about 1,000 \*\* flame which burned LPG and propane.

[0008]

[Problem(s) to be Solved by the Invention]With the decomposition art of the conventional PFC, since the drugs method cannot perform reuse of the drugs which reacted to PFC chemically, exchange of the expensive drugs consumed as consumable goods will become frequent, and operating cost will be 10 to 20 times the incineration method. The amount of drugs proportional to the PFC gas to process is required, and the device scale of practical use is as large as about 3-5-m<sup>2</sup> by an installation face product.

[0009]Since decomposition of not less than 1,000 \*\* and CF<sub>4</sub> is performed for decomposition of C<sub>2</sub>F<sub>6</sub> at a not less than 1,100 \*\* elevated temperature, a lot of thermal energies are required for a combustion system, and it also has generating of NOx by high temperature combustion, or a lot of CO<sub>2</sub>. Since PFC in a semiconductor manufacturing process is diluted and discharged by inactive N<sub>2</sub> gas, flame-failure potential is high and sufficient operation management is called for.

[0010]Application of a combustion system is considered to a semiconductor manufacturing process. Since PFC is discharged as mixed gas of several percent concentration diluted with N<sub>2</sub> gas, a lot of combustion air is needed for combustion of this mixed gas with fuel gas, and since the amount of raw gas increases as a result, a device scale serves as about 0.7-5-m<sup>2</sup> by

an installation face product greatly.

[0011]For example, when 1% of  $C_2F_6$  is contained in the exhaust gas of 100 l. / min from a semiconductor manufacturing process, LPG required to consider [ of pyrolysis temperature ] 1,000 \*\* as the above will serve as about 400 l. / min, if 10 l. / min, and a required air content set an excess rate to 1.5. Oxygen in the air is consumed, since  $CO_2$  carries out 30 l. / min generating, the total amount of exhaust gas after combustion serves as about 500 l. / min, and it increases by about 5 times the gas volume from a manufacturing process. A semiconductor plant has large restrictions of a space because of a clean room, and reservation in particular of a space when newly arranging a processing unit at an established factory is not easy.

[0012]On the other hand, although PFC and chemical composition are similar, to the chlorofluorocarbon of CFC (chloro-fluorocarbon) with an ozone-crack operation, or HCFC (hydroniumchloro-fluorocarbon), the catalyst method which starts decomposition at about 400 \*\* is used. Since CFC and HFC contain chlorine with a large atomic radius during a presentation, the molecular structure combined with fluoride and hydrogen with a small atomic radius becomes distorted, and, for this reason, decomposition at low temperature is attained comparatively.

[0013]However, since molecular structure of PFC was compact excluding chlorine and associative strength was strong, that decomposition temperature was as high as about 700 \*\*, and this catalyst method was not able to be applied. Recently, this invention persons have the reaction temperature of about 700 \*\*, succeed in development of an alumina system catalyst applicable also to decomposition of PFC, and have applied previously (Japanese Patent Application No. No. 4349 [ nine to ], Japanese Patent Application No. No. 163717 [ nine to ]). This invention is made by flue gas treatment with the application of this catalyst.

[0014]After a catalyst is used for the purpose of this invention, there is in providing the disposal method of the fault fluoride which can improve a decomposition reaction, and its processing unit.

[0015]

[Means for Solving the Problem]The feature of the 1st invention removes this silicon from exhaust gas containing fault fluoride and silicon, supplies it to a catalyst bed with which exhaust gas containing fault fluoride in which either water and a steam were added was filled up into a catalyst after that, and there is in disassembling fault fluoride according to a catalyst. Since silicon is beforehand removed from exhaust gas supplied to a catalyst, the 1st invention can prevent a particle produced by the reaction of water (or steam) added by exhaust gas and silicon in exhaust gas from closing PORASU formed in a catalyst. That a particle blockades a gap formed between catalysts can also prevent the 1st invention. For this reason, since the 1st invention can utilize surface area of a catalyst effectively, it can improve a decomposition reaction of fault fluoride. The 1st invention can improve decomposition efficiency of fault

fluoride.

[0016]The feature of the 2nd invention performs heating so that temperature of said exhaust gas may be not less than 650 \*\*. Preferably, since an alumina system catalyst is used, fault fluoride can be efficiently disassembled easily with reaction temperature of 650-750 \*\*.

[0017]There is the feature of the 3rd invention in removing acid gas from cooled exhaust gas. Acid gas contained in exhaust gas is remarkably reduced by this.

[0018]The feature of the 4th invention removal of silicon from exhaust gas, Within the 2nd silicon stripper, it is carried out using the 1st silicon stripper and the 2nd silicon stripper, supply exhaust gas discharged from the 1st silicon stripper to the 2nd silicon stripper, make water and exhaust gas contact them, and within the 1st silicon stripper, It is in contacting mixed water of cooling water which cooled exhaust gas, and wastewater discharged from the 1st silicon stripper and exhaust gas containing cracked gas.

[0019]Since mixed water of cooling water contacted with exhaust gas which contains wastewater and cracked gas which were discharged from the 1st silicon stripper within the 1st silicon stripper, and exhaust gas containing silicon are contacted, some silicon contained in exhaust gas is removed by the above-mentioned mixed water. For this reason, since quantity of the new water supplied in the 2nd silicon stripper decreases, a displacement processed decreases. Since silicon contained in exhaust gas is removed by the 1st silicon stripper and the 2nd silicon stripper, removal efficiency of silicon contained in exhaust gas improves.

[0020]Preferably, a warmer, a reactor, and a cooling system are considered as unification composition, and reduction of a miniaturization and heat loss is aimed at. Preferably, it is unification composition, and these consider it as a horizontal type arranged horizontally, and there are in having provided a baffle member which intercepts a flow of undecomposed fault fluoride in the upper part of a catalyst bed of a reactor. Thereby, a catalyst sediments caudad with the passage of time, and gas which passes through an opening produced in the upper part of a catalyst bed can be intercepted.

[0021]It is in having provided preferably a heat exchanger which performs heat exchange between exhaust gas and reaction water containing cracked gas between a reactor and a cooling system. Thereby, heating energy and a circulating water flow can be reduced by half.

[0022]The above-mentioned PFC processing unit is applied as a processing unit of exhaust gas after a dry etching process of a semiconductor plant, or a CVD cleaning process, and decomposition treatment of efficient PFC can be realized. Concentration of PFC in exhaust gas of an exit of a PFC processing unit or an entrance, and an exit is measured, a management tool which supervises a processing situation is established, and soundness, catalyst exchange time, etc. of processing are checked. A space problem when attaching to an established factory is solvable by arranging the above-mentioned unification, especially a PFC processing unit of a horizontal type in duct area of a semiconductor plant.

[0023]Although PFC as used in the field of this invention contains chlorofluocarbon of FC and HFC, nitrogen trifluoride ( $NF_3$ ), sulfur hexafluoride ( $SF_6$ ) which are fault fluoride and do not contain chlorine, it points out fault fluoride shown in Table 1 currently substantially used by a semiconductor plant.

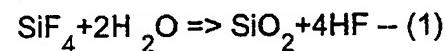
[0024]

[Embodiment of the Invention]Hereafter, two or more examples applied to the flue gas treatment from a semiconductor manufacturing process are described in detail about the PFC processing unit using the catalyst of this invention. The same numerals are given for the drawing of each example to the through and equivalent component.

[0025][Example 1] Drawing 1 shows the PFC processing unit which decomposes  $CF_4$  and is removed out of exhaust gas. As opposed to the exhaust gas containing the etching gas ( $CF_4$ ) from the semiconductor manufacturing process in which the PFC processing unit 1 of this example has a dry etching process, The introduction spray 11, exhaust gas, and water which pour impurity removal are introduced. It consists of the warmer 12 to heat, the reactor 13 which is filled up with the catalyst bed 14 and hydrolyzes  $CF_4$ , the cooling system 16 which cools cracked gas and is made to dissolve  $CO_2$  etc. in water, and the stripper 17 which removes the acid gas under exhaust air. Especially in the following, the treatment process of the warmer 12, the reactor 13, and the cooling system 16 may be called a PFC decomposition treatment part.

[0026] $SiF_4$  etc. which were generated by etching with about 1 vol% of  $CF_4$  which was not consumed by an etching process are contained in the exhaust gas from a semiconductor manufacturing process as an impurity. In order to prevent the blockade and degradation of the catalyst bed 14 by this impurity, the exhaust gas which went via the vacuum pump 21 is introduced into the introduction spray (silicon removal machine) 11 by the piping 3. Water is poured into the water supplied from the piping 37 continuously in the container of the introduction spray 11 by the spray 2, and  $SiF_4$  in exhaust gas is decomposed into  $SiO_2$  and HF by the reaction of (1) type.

[0027]



Since  $SiO_2$  is solid particles, it is removed from exhaust gas by the water by which the spray was carried out simultaneously with generation. Since the solubility to water is large, HF is removable from exhaust gas similarly. The effluent containing  $SiO_2$  and HF which were discharged from the introduction spray 11 is processed as waste fluid led to the pars basilaris ossis occipitalis of the stripper (acid gas stripper) 17 through the piping 75. Removal of the impurity currently accompanied to exhaust gas may be contacted in water not by a spray but

by a bubbling method.

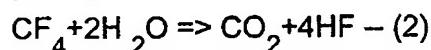
[0028] It is mixed with the water for a reaction (or steam) supplied from the piping 35, and the exhaust gas containing  $\text{CF}_4$  after removing an impurity is introduced into the warmer 12 for the piping 4. Supply of the water (or steam) to the inside of exhaust gas is because the reaction of  $\text{CF}_4$  in the catalyst bed 14 serves as  $\text{CF}_4$  and hydrolysis by  $\text{H}_2\text{O}$ . The supply flow rate of reaction water (or steam) will be about 25 times to 1 mol of  $\text{CF}_4$ .

[0029] The warmer 12 heats exhaust gas by the indirect heating by the electric heater 32 to the temperature which is about 700 \*\* which decomposition of  $\text{CF}_4$  starts by the catalyst bed 14.

The temperature controller 30 adjusts the current of the electric heater 32 based on emission temperature  $T_e$  measured with the thermometer 31 arranged at the entrance of the reactor 13, and it carries out temperature control so that the reaction temperature in the catalyst bed 14 may be maintained. In  $\text{CF}_4$ , it is heated by about 650-750 \*\*.

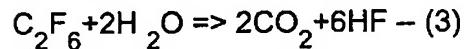
[0030] The exhaust gas containing heated  $\text{CF}_4$  is supplied to the reactor 13 with which it filled up with the catalyst. The catalyst bed 14 is filled up with the catalyst of the below-mentioned alumina ( $\text{aluminum}_2\text{O}_3$ ) system, and  $\text{CF}_4$  reacts to  $\text{H}_2\text{O}$  like (2) types, and is decomposed into HF and  $\text{CO}_2$ .

[0031]



When PFC contained in exhaust gas is  $\text{C}_2\text{F}_6$ , it reacts like (3) types and decomposes into  $\text{CO}_2$  and HF.

[0032]



Drawing 2 is the decomposition characteristic of PFC by an alumina system catalyst, reaction temperature is shown on a horizontal axis and cracking severity is shown on the vertical axis by it. This characteristic is the one above-mentioned example of point \*\*, and  $\text{aluminum}_2\text{O}_3$  is

[ $\text{NiO}_2$  of the presentation of the used catalyst] 20% 80%. Four sorts of PFC(s),  $\text{CHF}_3$ ,  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ , and  $\text{C}_4\text{F}_8$ , were used for sample offering gas. A test condition is 1000/h about SV 0.5% in PFC gas concentration. About 10 times of the theoretical value were added as reaction water. As shown in drawing 2, nearly 100 cracking severity is acquired for four sorts of PFC(s) with the reaction temperature of about 700 \*\*. At  $\text{CF}_4$  and  $\text{CHF}_3$ , it is the cracking severity of not less than 80% at about 670 \*\* not less than 95% in about 650 \*\* in  $\text{C}_2\text{F}_6$  and  $\text{C}_4\text{F}_8$ .

According to this catalyst, practical decomposition of PFC is attained with the reaction

temperature of about 650-750 \*\*.

[0033]With the water continuously supplied by the sprays 6 and 7 of the cooling system 16, the hot exhaust gas containing CO<sub>2</sub> and HF which were discharged from the catalyst bed 14, and which are cracked gas cools temperature at 100 \*\* or less, and is introduced into the stripper 17. Supply of the cooling water to the sprays 6 and 7 is performed by the piping 38 and 39. Without being based on a spray, in a tank, bubbling of the hot exhaust gas may be carried out, and it may cool. From the sprays 6 and 7, an alkali solution may be supplied instead of water. A part of HF is absorbed and removed by the cooling water injected from the sprays 6 and 7. The waste fluid discharged from the cooling system 16 is led to the pars basilaris ossis occipitalis of the stripper 17 by the piping 8 and 75.

[0034]the stripper 17 – the inside of exhaust gas -- about 4 vol(s)% -- in order to remove high-concentration HF contained, water is continuously supplied to the packed bed 10 which packed the RAHISHI ring made from a plastic from the spray 36, it is fully contacting water and cracked gas, and HF is reduced from 4% to several ppm. Supply of the water to the spray 36 is performed by the piping 76. The detoxicated cracked gas is discharged by the piping 43 out of a system via the fan 22.

[0035]HF etc. which are maintained by negative pressure and contained in exhaust gas by the fan 22 are prevented from revealing the inside of the cooling system 16 and the stripper 17 out of a system. A bubbling method is possible also for the stripper 17. However, the direction of a spray method or a packed column method has little pressure loss, and can make the fan for exhaust air small.

[0036]The waste fluid which, on the other hand, contains the impurity and HF which were discharged from the introduction spray 11, the cooling system 16, and the stripper 17 is led to the neutralization processing unit which is not illustrated through the piping 42 by the drive of the drain pump 23, and waste water treatment is carried out.

[0037]In the introduction spray 11 whose this example is a silicon removal machine, since the silicon contained in exhaust gas is beforehand removed as SiO<sub>2</sub>, particles, such as SiO<sub>2</sub>, are not carried into the catalyst bed 14 of the reactor 3. When not installing the introduction spray 11, with the water supplied from the piping 35, from the juncture of the piping 4 and the piping 35, the reaction of (1) type arises in the downstream and SiO<sub>2</sub> is generated. When this SiO<sub>2</sub> flows in the catalyst bed 14, the problem of following \*\* and \*\* is produced. \*\* SiO<sub>2</sub> closes PORASU formed in the catalyst. \*\* Blockade the gap formed between catalysts. \*\* And originate in \*\*, the surface area of a catalyst decreases, and the decomposition reaction of PFC falls. It originates in \*\*, the flow of the exhaust gas between catalysts worsens, and contact of a catalyst and exhaust gas is checked. This also leads to the fall of the decomposition reaction of PFC. Since this example generates the reaction of (1) type

compulsorily in the introduction spray 11 and removes SiO<sub>2</sub> from exhaust gas a priori, the above-mentioned problem does not arise and it can improve the decomposition efficiency of PFC. Using a catalyst, this example can be efficient, can realize decomposition treatment of PFC, and can avoid discharge into the atmosphere of PFC which is one of the cause gas of global warming.

[0038]According to this example, decomposition of CF<sub>4</sub> is attained at a temperature lower enough than the conventional combustion system, and there are also few utilities, such as thermal energy and water, and they end. In the case of a chip fabrication factory, it is advantageous also from the safety aspect to a fire that cracked gas temperature is low. Since a life is possible also for reuse for a long time, the catalyst can reduce operating cost substantially compared with a drugs method.

[0039]Although the above-mentioned example was aimed at the case where a chip fabrication factory adopts CF<sub>4</sub> as the raw gas of an etching process, it is not restricted to this. For example, the exhaust gas in the case of adopting C<sub>2</sub>F<sub>6</sub> as cleaning gas by CVD can also be processed with the same composition. In addition, it can process with the same composition and the reaction temperature of around about 700 \*\* to PFC shown in Table 1.

[0040][Example 2] The PFC decomposition treatment part which made unification composition the PFC decomposition treatment part of Example 1 is shown in drawing 3. The warmer 12, the reactor 13, the cooling system 16, and the heat exchanging room 15 are combined in one by the flanges 121,131 and 161. The warmer 12, the reactor 13, and the heat exchanging room 15 are carrying out the inner package of the heat insulating material 122,132,152, respectively. According to this PFC decomposition treatment part, a processing unit can be miniaturized and the response of control by the temperature controller 30 can also be improved. Heat loss can be reduced compared with the case where piping connection of between each apparatus is carried out. Unification composition without the heat exchanging room 15 may be used.

[0041]Since the inside of a semiconductor plant serves as a clean room where air conditioning management of the whole building was carried out, in order to lessen floor area of the whole factory, to make the installing space of apparatus small is desired. According to the PFC decomposition treatment part in this example, an installation area becomes about 0.4-m<sup>2</sup> with a PFC gas processing unit provided with the exhaust gas throughput about [ containing about 1% of CF<sub>4</sub> ] 100 l. / min. It is to [ 1/several ] about [ of the installation area at the time of assuming that a combustion system and a drugs method are used for this ] 1/10.

[0042]In this example, the heat exchanging room 15 which uses effectively the heat of about 700 \*\* exhaust gas discharged from the reactor 13 is formed between the reactor 13 and the

cooling system 16. In the heat exchanging room 15, the heat exchanger tube 151 connected to the piping 35 which supplies reaction water is installed. Reaction water serves as a steam within the heat exchanger tube 151, and this steam is led to the entrance side of the warmer 12 by the piping 153.

[0043] Drawing 4 shows the PFC processing unit 1C with which PFC decomposition treatment part application of the unification composition shown in drawing 3 was carried out. Low-temperature reaction water (it supplies for the piping 35) flows into the entrance of the heat exchanger tube 151. Heat exchange of this reaction water is carried out to about 700 \*\* exhaust gas in the heat exchanging room 15, it serves as a not less than 100 \*\* steam, and is introduced into the warmer 12 by the piping 153. On the other hand, by the heat exchange, it is cooled by about 300 \*\* or less, and exhaust gas is led to the cooling system 16. Since heat exchange is performed between reaction water and hot cracked gas, recovery of thermal energy is attained and can reduce by half amount of water required for energy and cooling required for heating, respectively.

[0044] [Example 3] Drawing 5 shows the exhaust air managerial system of the semiconductor plant which applied the PFC processing unit 1. The PFC processing unit 1 is connected to the three dry etching systems 5, respectively. The gas chromatograph 40 measures concentration, such as PFC in the exhaust gas extracted from the entrance side and outlet side of each PFC processing unit 1, for example,  $\text{CF}_4$  etc., and is transmitting each measured value to the monitoring instrument 45. The acid gas removal filter 41 is formed in the gas sampling pipe 46A from an entrance side.

[0045] This system is explained concretely. Each dry etching system 5 supplies  $\text{CF}_4$  which is one sort of PFC gas to an inside as etching gas, and is performing the etching process to a wafer, respectively. The exhaust gas of each dry etching system 5 is led to the PFC processing unit 1 which reaches and corresponds to the piping 29 through the piping 44A and 44B by the drive of the vacuum pumps 21A and 21B. The exhaust gas contains about 1 vol% of  $\text{CF}_4$  which was not consumed by an etching process, and  $\text{SiF}_4$  generated by etching. After exhaust gas is processed with the PFC processing unit 1, it is exhausted by the acid duct (exhaust duct) 25 through the piping 43. A part of exhaust gas in the piping 3 is led to the gas chromatograph 40 by the gas sampling pipe 46A and the acid gas filter 47, respectively. By the gas sampling pipe 46B, the exhaust gas in the piping 43 is also led to the gas chromatograph 40, respectively.  $\text{CF}_4$  concentration in the exhaust gas supplied to each PFC processing unit 1 and the exhaust gas discharged from each PFC processing unit 1 is measured by the gas chromatograph 40. The monitoring instrument 45 inputs the measured value of  $\text{CF}_4$  concentration from the gas chromatograph 40. When the monitoring instrument 45 has  $\text{CF}_4$

concentration higher than the 1st preset value in a certain piping 43, it generates a warning sound, blinking the alarm 51 of the PFC processing unit 1 applicable for the notice of an abnormal occurrence. It makes a warning sound emit, when the monitoring instrument 45 has CF<sub>4</sub> concentration higher than the 2nd preset value in a certain piping 29, blinking the alarm 50 of the dry etching system 5 applicable for the notice of an abnormal occurrence.

[0046]The PFC concentration in the exhaust gas with which this example is supplied to the PFC processing unit 1, and the PFC concentration discharged by un-decomposing from the exit are measured every device 5. From this result, the monitoring instrument 42 supervises the PFC concentration of exit exhaust air of the processing unit 1, and when the desired value is not fulfilled, it outputs a display or an alarm. The exchange time by the soundness or catalyst de-activation of catalytic reaction is checked from the cracking severity by the PFC concentration of the entrance side of the PFC processing unit 1, and an outlet side.

[0047][Example 4] Drawing 6 shows the layout of the semiconductor plant. The building 59 of the semiconductor plant also serves as the upper part and a lower part with the clean rooms 53 and 54 from the grating 52. The air in the clean room 54 is purified by the drive of Blois 55A and 55B with the filters 55A and 55B, and is led to the clean room 53 for the piping 57A and 57B by it. This air is again purified by the filter 58. The clean room 53 has an air cleanliness class higher than the clean room 54. The dry etching system 5 is installed in the clean room 53 which is manufacturing installation area. The clean room 54 serves as the piping duct area 102 which lets the auxiliary machinery area 103 in which the vacuum pumps 21A and 21B etc. are installed, piping, and ducts pass.

[0048]This example arranges two-set processing unit [ of PFC(s) ] 1' in the duct area 102. The acid duct 25 is installed in the duct area 102, and the exhaust gas containing acid gas is led to an acid gas processing unit (not shown), and is processed by the acid duct 25. Therefore, PFC processing unit 1' of this example omits the stripper 17 of the last stage of the above-mentioned PFC processing unit 1, and exhausts directly the exhaust gas containing HF after cooling, etc. into the acid duct (exhaust duct) 25.

[0049]According to this, also in the existing established semiconductor plant difficult for reservation of a space, installation of a PFC processing unit becomes easy. In this case, since height measurement is generally small the duct area 102, if it is made sideways long and slender like a graphic display of PFC processing unit 1', the arrangement to the duct area 102 will become easier in many cases.

[0050]The structure of PFC processing unit 1' of a horizontal type is shown in drawing 7. It is considered as the structure which put each apparatus in order horizontally and was unified to the vertical mold structure of drawing 3. If the flow of the introduction spray 11 and the spray of the cooling system 16 is performed downward from a top, there will be no place which changes functionally also by horizontal-type arrangement. However, when the catalyst bed 14 is made

sideways, if time passes, a catalyst will sediment slightly, an opening will be produced in the upper part of the catalyst bed 14, and there is a possibility that the processing-object gas (PFC gas) in which this opening is not decomposed may pass. Then, the baffle plate 141 is formed in the upper part of the catalyst bed 14. The pressure plate 142,143 of the perforated plate which presses down the transverse movement of a catalyst is installed in the entrance side and outlet side of the reactor 13. As shown in drawing 7 (b), the sector baffle plate 141 shall be arranged in the upper part of the catalyst bed 14 on a cylinder, and the sector height shall cover the maximum opening width by subsidence. The gas which passes through that with this baffle plate 141 even if an opening produces in the catalyst bed 14 upper part during operation can be intercepted, and all processing-object gas passes the catalyst bed 14, and is decomposed.

[0051]According to this example, in the established chip fabrication factory which does not have a margin in the disposition space of apparatus, installation of a PFC processing unit can be made easy and it can respond to the future near control of exhaust gas for global warming prevention by using the piping duct area 102. The vertical mold (drawing 3) and horizontal type (drawing 7) of a PFC processing unit are suitably chosen according to the situation of the space of an application place.

[0052][Example 5] The PFC processing unit 1B which are other examples of this invention is shown in drawing 8. The PFC processing unit 1B changes the introduction spray 11 of the PFC processing unit 1 to the silicon stripper 11A which is an introduction spray, and is newly provided with the return pipe 60. The silicon stripper 11A is provided with the silicon removal machines 11B and 11C. The silicon removal machine 11B installs the spray 2A in a container. The silicon removal machine 11C installs in a container spray 2B and the diffused part 59 which covered with packing. The container of the silicon removal machines 11B and 11C comprises corrosion-resistant vinyl chloride, in order to prevent the corrosion by HF. It is connected to the piping 42 by the downstream of the drain pump 23, and, moreover, the return pipe 60 is connected to spray 2B. The piping 37 is connected to the spray 2A.

[0053]The exhaust gas with which  $\text{CF}_4$ ,  $\text{SiF}_4$ , etc. are contained as an impurity is discharged by the piping 3 in the container of the silicon removal machine 11C. Exhaust gas goes up the inside of a container, passes the diffused part 59, diffuses the inside of a container and comes to flow through it. Some wastewater breathed out from the drain pump 23 is injected from spray 2B through the return pipe 60. The concentration of F ion under wastewater breathed out from the drain pump 23 and Si ion is tens of ppm or less. This wastewater fully has the removal performance of Si and HF. The reaction of (1) type arises by contact with the wastewater by which the spray was carried out to a part of  $\text{SiF}_4$  contained in exhaust gas.

Generated  $\text{SiO}_2$  is removed from exhaust gas by wastewater. HF dissolves in wastewater.

[0054]The exhaust gas discharged from the silicon removal machine 11C is led to the silicon removal machine 11B. The new water supplied from the piping 37 is injected in the silicon removal machine 11B from the spray 2A. In the silicon removal machine 11B, the reaction of (1) type arises by contact with the water by which the spray was carried out to  $\text{SiF}_4$  which remains in exhaust gas. The effluent of the silicon removal machine 11B containing  $\text{SiO}_2$  and HF is led to the silicon removal machine 11C, and is led to the pars basilaris ossis occipitalis of the stripper 17 through the piping 41 with the effluent injected from spray 2B. Processing in other portions of the PFC processing unit 1B is the same as processing with the PFC processing unit 1.

[0055]The PFC decomposition treatment part of the PFC processing unit 1B has the composition which unified the PFC decomposition treatment part of the PFC processing unit 1. The composition of the PFC decomposition treatment part of the PFC processing unit 1B is explained using drawing 9.

[0056]The PFC decomposition treatment part in this example unifies the warmer 12, the reactor 13, and the cooling system 16. The casing 62 and the inner tube 63 are shared by the warmer 12 and the reactor 13. The inside diameter of the inner tube 63 is small above the lower part. The flange 66 of the inner tube 63 is fixed to the flange 68 of the casing 62 with a bolt. The warmer 12 and the reactor 13 are integral construction. The annular plate 64 is installed in the upper part of the inner tube 63. Rather than the annular plate 64, the warmer 12 is located up and has the wrap thermal insulation 122 for the electric heater 32 and this. The gap 73 is formed between the casing 62 and the annular plate 64. The gap 73 prevents it from the heat of hot (700 \*\*) exhaust gas being transmitted from the inner tube 63 and the annular plate 64 to the casing 62, and being emitted outside. That is, the heating loss of exhaust gas can be decreased.

[0057]The reactor 13 is caudad located rather than the annular plate 64. The reactor 13 is provided with the catalyst cartridge 65 which has the catalyst bed 14 filled up with an alumina system catalyst on the wire gauze 74. An alumina system catalyst is a catalyst containing aluminum<sub>2</sub>O<sub>3</sub> 80% and NiO<sub>2</sub> 20%. The catalyst cartridge 65 is inserted into the inner tube 63.

The cylinder 70 is attached to the casing 62 by combining the flange 69 with the flange 68. The catalyst cartridge 65 is held by engaging the flange 67 with the flange 68 at the casing 62. The reactor 13 has the heater for incubation (not shown) installed between the casing 62 and the inner tube 63. The baffle attachment component 71 which has the baffle 72 is attached to the cylinder 70. The cooling system 16 is located under the baffle attachment component 71, and is attached to this. Air is supplied by the piping 61 in the warmer 12.

[0058]The warmer 12 in this example, the reactor 13, and the cooling system 16 exhibit the same function as them of the PFC processing unit 1.

[0059]The PFC processing unit 1B produces the effect acquired with the PFC processing unit 1. Since the quantity of the new water in which the PFC processing unit 1C is supplied from the water supply piping 38 decreases, the displacement led to a neutralization processing unit (not shown) decreases. Since the reaction of (1) type arises at two places of the silicon removal machines 2 and 72, the removal efficiency of Si components, such as  $\text{SiF}_4$  contained in exhaust gas, improves. Since the passage which draws exhaust gas in the cooling system 16 from the inside of the baffle attachment component 71 winds by installation of the baffle 72, the droplet of the cooling water injected from the sprays 6 and 7 can be prevented from reaching the catalyst bed 14. For this reason, since the temperature fall of the catalyst bed 14 by that droplet can be prevented, discharge of undecomposed PHC is lost.

[0060]In the composition of drawing 8, direct continuation of the return pipe 60 may be carried out to the pars basilaris ossis occipitalis of the stripper 17 instead of the piping 42. In this case, it is necessary to install the pump for supplying waste fluid to spray 2B in the return pipe 60. Also in such composition, the same effect as the composition of drawing 8 can be acquired.

[0061]

[Effect of the Invention]Since the surface area of a catalyst is effectively utilizable according to the 1st invention, the decomposition reaction of fault fluoride can be improved and the decomposition efficiency of fault fluoride can be improved.

[0062]According to the 2nd invention, the large fault fluoride of the warming effect can be efficiently disassembled easily with the reaction temperature of not less than (preferably 650-750 \*\*) 650 \*\*, and global warming can be controlled.

[0063]According to the 3rd invention, the acid gas contained in exhaust gas can decrease remarkably, and the quantity of the acid gas (for example, HF) emitted into the atmosphere decreases remarkably.

[0064]According to the 4th invention, since the quantity of the new water used for removal of silicon decreases, the quantity of the wastewater to process can be decreased. Since the 1st silicon stripper and the 2nd silicon stripper remove silicon, the removal efficiency of the silicon contained in exhaust gas improves remarkably.

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[Translation done.]

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**DESCRIPTION OF DRAWINGS**

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**[Brief Description of the Drawings]**

[Drawing 1]It is a lineblock diagram of the PFC processing unit which is one suitable example of this invention.

[Drawing 2]It is a characteristic figure showing the cracking severity of PFC by an alumina system catalyst.

[Drawing 3]It is a lineblock diagram showing an example (vertical mold) of the PFC decomposition treatment part of integrated structure.

[Drawing 4]It is a lineblock diagram of the PFC processing unit which are other examples of this invention which applied the PFC decomposition treatment part of drawing 3.

[Drawing 5]It is an exhaust air managerial system lineblock diagram of the semiconductor manufacturing device which applied the PFC processing unit of drawing 1.

[Drawing 6]It is an explanatory view showing the layout of the outline of the semiconductor plant which has arranged the PFC processing unit of drawing 7.

[Drawing 7]It is drawing of longitudinal section in the direction in which the composition of the PFC processing unit which are other examples of this invention is shown, (a) goes to outline drawing of longitudinal section of a PFC processing unit direct, and (b) goes to the shaft orientations of the PFC processing unit near [ baffle plate 141 ] (a) direct.

[Drawing 8]It is a lineblock diagram of the PFC processing unit which are other examples of this invention.

[Drawing 9]It is a detailed lineblock diagram of the PFC decomposition treatment part of drawing 8.

**[Description of Notations]**

1, 1', 1C, 1 B--PFC processing unit, 2 and 2A, 2B, 6, 7, 36 -- Spray, 5 -- A dry etching system, 11 -- An introduction spray, 11A -- Silicon stripper, 11B, 11C [ -- Catalyst bed, ] -- A silicon removal machine, 12 -- A warmer, 13 -- A reactor, 14 15 [ -- Vacuum pump, ] -- A heat

exchanging room, 16 -- A cooling system, 17 – A stripper, 21 22 [ -- Temperature controller, ] - - A fan, 23 -- A drain pump, 25 -- An acid duct, 30 31 [ -- An acid gas removal filter 60 / -- A return pipe, 72 / -- A baffle return pipe, 101 / – Manufacturing installation area, 102 / -- Piping duct area, 103 / -- Auxiliary machinery area, 141 / -- A baffle plate, 151 / -- Heat exchanger tube, ] – A thermometer, 32 -- An electric heater, 40 -- A gas chromatograph, 41

[Translation done.]

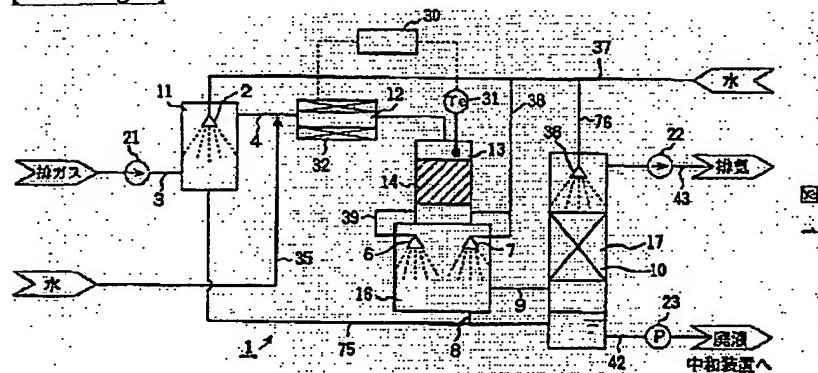
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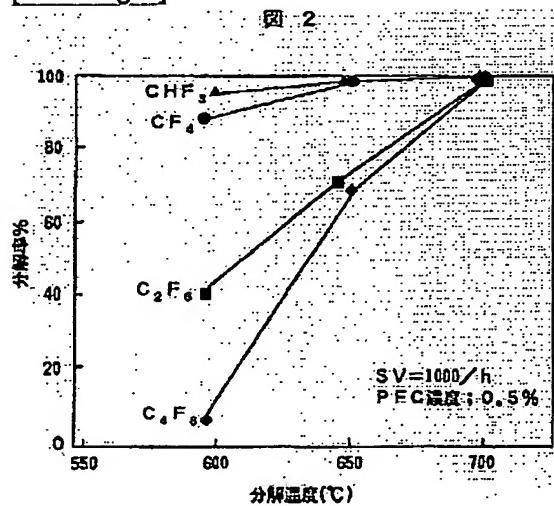
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## DRAWINGS

[Drawing 1]



[Drawing 2]



[Drawing 3]

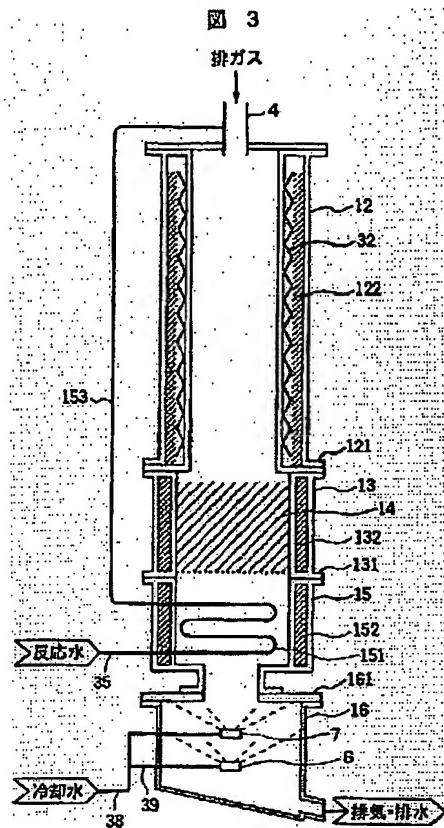
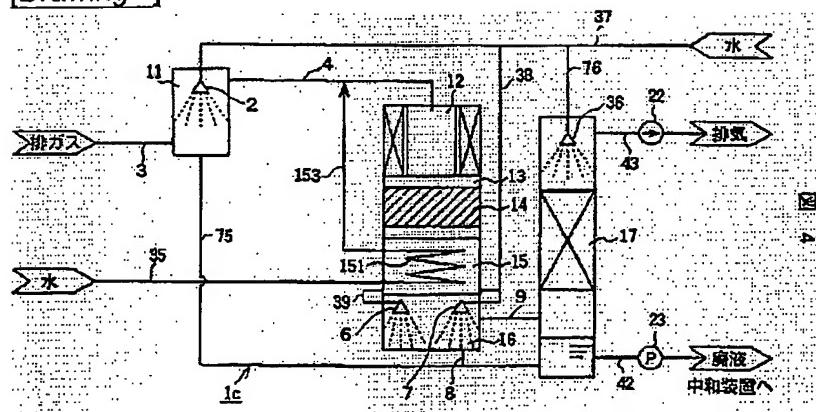
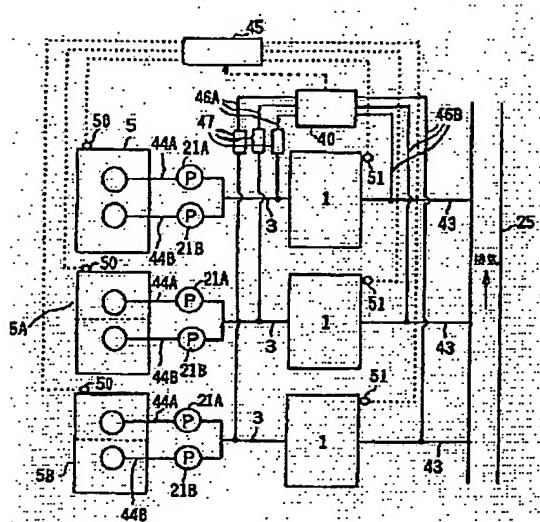
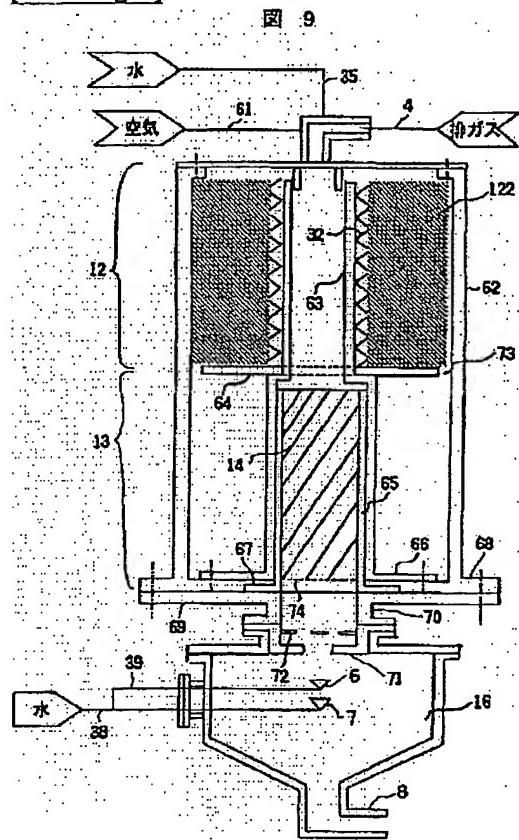
**[Drawing 4]****[Drawing 5]**

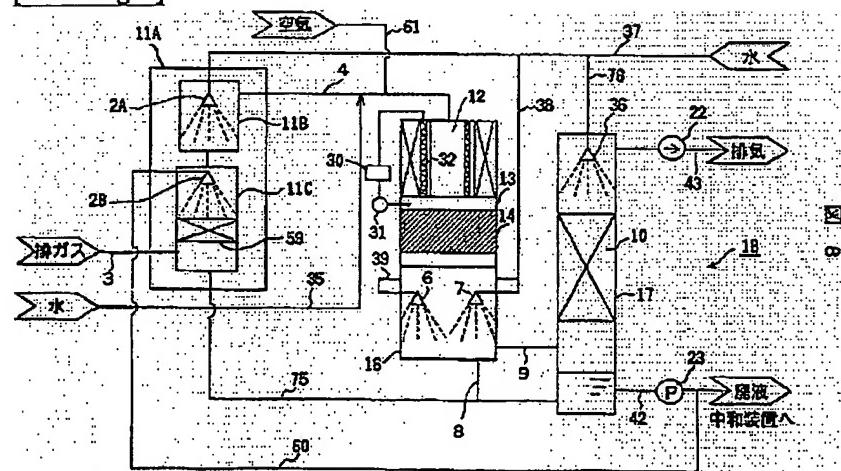
図 5



[Drawing 9]



[Drawing 8]




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CORRECTION OR AMENDMENT

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B01D 53/34 134 E

ZAB

134 C

53/36 G

[A written amendment]

[Filing date] January 9, Heisei 13 (2001.1.9)

[The amendment 1]

[Document to be Amended]Specification

[Item(s) to be Amended]Claim

[Method of Amendment]Change

[Proposed Amendment]

[Claim(s)]

[Claim 1]A disposal method of fault fluoride which disassembles said fault fluoride which heated said exhaust gas containing said fault fluoride which removed silicon from exhaust gas containing fault fluoride and silicon, and in which either water and a steam were added, supplied it to a catalyst bed with which a catalyst was filled up, and was contained in said exhaust gas according to said catalyst.

[Claim 2]A disposal method of fault fluoride of claim 1 which cools exhaust gas containing cracked gas produced by disassembly of said fault fluoride.

[Claim 3]A disposal method of fault fluoride of claim 1 which performs said heating so that temperature of said exhaust gas may be not less than 650 \*\*.

[Claim 4]A disposal method of fault fluoride of claim 3 in which said exhaust gas is heated by range which are 650 \*\* - 750 \*\*.

[Claim 5]A disposal method of fault fluoride of claim 2 which removes acid gas from said cooled exhaust gas, or claim 3.

[Claim 6]A disposal method of fault fluoride of claim 1 which performs removal of silicon from said exhaust gas by contacting exhaust gas and water containing said silicon, or claim 2.

[Claim 7]A disposal method of fault fluoride of claim 6 which performs cooling of exhaust gas containing said cracked gas by contact with said exhaust gas and cooling water.

[Claim 8]A disposal method of fault fluoride of claim 7 to which mixed water of said cooling water which cooled exhaust gas is contacted characterized by comprising the following. Removal of silicon from said exhaust gas is performed using the 1st silicon stripper and the 2nd silicon stripper, Said exhaust gas discharged from said 1st silicon stripper is supplied to said 2nd silicon stripper, water and said exhaust gas are contacted within said 2nd silicon stripper, and it is said exhaust gas within said 1st silicon stripper.

Wastewater discharged from said 2nd silicon stripper, and said cracked gas.

[Claim 9]A disposal method of fault fluoride of claim 1 in which said catalyst is an alumina system catalyst.

[Claim 10]A disposal method of fault fluoride of either claim 1 which is the exhaust gas with which said exhaust gas was discharged from a semiconductor manufacturing device thru/or claim 9.

[Claim 11]A fault fluoride processing unit comprising:

A silicon stripper which removes this silicon from exhaust gas containing fault fluoride and silicon.

Heating apparatus which heats said exhaust gas with which it was discharged from said silicon stripper, and either water and a steam were added.

A catalyst bed with which a catalyst which disassembles said fault fluoride which was heated with said heating apparatus, and which was contained in said exhaust gas was filled up.

[Claim 12]A fault fluoride processing unit of claim 11 provided with a cooling system which cools said exhaust gas discharged from said catalyst bed.

[Claim 13]A fault fluoride processing unit of claim 12 characterized by comprising the following.  
A thermometric element which detects temperature of said exhaust gas supplied to said catalyst bed.

A control device which controls said heating apparatus based on measurement temperature of this thermometric element.

[Claim 14]A fault fluoride processing unit of claim 12 provided with an acid gas stripper which removes acid gas contained in said exhaust gas discharged from said cooling system.

[Claim 15]A fault fluoride processing unit of claim 11 or claim 12 by which a water supply pipe which supplies water in contact with said exhaust gas is connected to said silicon stripper.

[Claim 16]A fault fluoride processing unit of claim 15 provided with a spray device with which said cooling system carries out the spray of the cooling water which cools said exhaust gas.

[Claim 17]The 1st silicon stripper to which said exhaust gas is supplied to said silicon stripper, It has the 2nd silicon stripper to which said exhaust gas discharged from said 1st silicon stripper is supplied, A wastewater feed pipe which supplies wastewater discharged from said cooling system is connected to said 1st silicon stripper, A fault fluoride processing unit of claim 12 or claim 14 with which a water supply pipe which supplies water is connected to said 2nd silicon stripper, and said water in said 2nd silicon stripper is supplied to said 1st water supplying device from said 2nd silicon stripper.

[Claim 18]A fault fluoride processing unit of claim 11 which made integral construction said warmer, a reactor which contains said catalyst bed, and said cooling system at this order.

[Claim 19]A fault fluoride processing unit of claim 11 which provided a heat exchanger which performs heat exchange between exhaust gas and water which were discharged from said catalyst bed, and generates said steam between said catalyst bed and said cooling system.

[Claim 20]A fault fluoride processing unit of either claim 11 thru/or claim 19 in which said catalyst with which said catalyst bed was filled up is an alumina system catalyst.

[Claim 21]A flue gas treatment apparatus of a semiconductor manufacturing device characterized by comprising the following.

A silicon stripper which removes this silicon from exhaust gas containing fault fluoride and silicon which were discharged from a semiconductor manufacturing device.

Heating apparatus which heats exhaust gas containing said fault fluoride in which it was discharged from said silicon stripper, and either water and a steam were added.

A catalyst bed with which a catalyst which disassembles fault fluoride contained in said exhaust gas heated with said heating apparatus was filled up.

A cooling system which cools said exhaust gas discharged from said catalyst bed.

[Claim 22]A flue gas treatment apparatus of a semiconductor manufacturing device of claim 21 which installed said warmer which made integral construction said warmer, a reactor which contains said catalyst bed, and said cooling system at this order, and was made into integral construction, said reactor, and said cooling system in a building in which said semiconductor manufacturing device is installed.

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[Translation done.]